

# PRELIMINARY RESULTS ON THE MOLECULAR STRUCTURES OF THE ATHABASCA AND COLD LAKE ASPHALTENES

Jonathan P. Mathews\*, Semih Eser\*, and Parviz-Rahimi\*

\* The Energy Institute, College of Earth and Mineral Sciences, The Pennsylvania State University, University Park, PA 16802

\* National Center for Upgrading Technology, Suite A202, 1 Oil Patch Drive, Devon, Alberta, Canada, T9G 1A8

Keywords: Asphaltene structure, high-resolution mass spectroscopy

## INTRODUCTION

Asphaltene research has recently undergone a significant revitalization to facilitate utilization of heavier crude oils and to develop the massive oil sand reserves in Canada. The average chemical properties of natural asphaltenes tend to fall in a narrow range despite wide variations in their chemical behavior. In other words, the average bulk parameters of asphaltenes do not necessarily provide useful information for upgrading and behavioral studies. The final objective of this study is to generate molecular models for asphaltenes from two different sources, Cold Lake and Athabasca, to understand the differences in their molecular composition. These two asphaltenes give similar average structural parameters, yet behave quite differently (carbonization yields). Analysis by high-resolution laser pyrolysis indicated a distribution of molecular masses (100 to 1,500 AMU). Elemental compositions of these peaks will provide the input for molecular models without the need for extensive "averaging" of bulk parameters, thus, better indicating some of the structural diversity within the asphaltenes.

## EXPERIMENTAL

Pentane asphaltenes from Athabasca and Cold Lake bitumens were prepared using 40:1 solvent to sample ratios. Briefly, 10 g bitumen was placed in a flask and 400 mL of n-pentane was added. The flask was placed in an ultrasonic bath for 45 min and left to settle overnight at room temperature. The mixture was then placed in an ultrasonic bath again for 30 min and the asphaltenes were filtered using a medium porosity (10-15  $\mu$ m) fritted glass disk. The solid asphaltenes were rinsed with excess pentane until the washing was clear. To ensure that asphaltenes were free from residual maltenes, the collected asphaltenes were mixed with 50 mL of n-pentane, sonicated and filtered as before. Asphaltenes were then dried under vacuum at 45°C for 3 h.

Elemental analysis including C, H, S and N contents were determined using Perkin Elmer 2400 and O was determined using Carlo Erba 1104. Molecular weights of asphaltenes were determined in o-dichlorobenzene at 120°C using VPO.

Coking potential was obtained using a modified Conradson carbon residue test(1) utilizing a TGA instead of the prescribed glass sample vial. The results are not directly comparable to the Conradson method, as secondary cracking and mass transfer will significantly differ and hence underestimate the coke yield potential. Briefly  $5 \pm 0.5$  mg of sample was heated from 30 °C to 400 °C at 15 °C/min under nitrogen. The temperature has held constant for 90 minutes. The weight remaining was attributed to coke and ash. Ash was determined by heating the sample to 600 °C and changing the atmosphere to air, the remaining mass after 10 minutes was attributed to ash.

Mass spectra were acquired on a PerSeptive Biosystems Voyager-DE STR mass spectrometer using 337 nm light from a pulsed nitrogen laser for ionization. High-resolution results were obtained using reflector mode. Samples were prepared by dissolving approximately 50 micrograms of material in 500 ml of THF. Aliquots of 0.5 ml were deposited on the gold-plated target, and the solvent allowed to evaporate under ambient laboratory conditions. Samples were introduced into the mass spectrometer and analyzed as soon as possible to minimize evaporation of more volatile components. Ionization was conducted using laser setting slightly above the threshold for ionization. A total of 256 laser shots acquired over numerous sites within each sample were averaged. Calculated elemental analysis for mass spectral fragments where calculated using the non-weighted averages of 10 major peaks spanning 100 AMU's.

## RESULTS AND DISCUSSION

Unfortunately, asphaltene structural research is hampered by the use of the term "asphaltene" to describe such diverse structural entities as naturally occurring asphaltenes (from coal, crude and oil sands),  $C_5$ ,  $C_6$  and  $C_7$  "cuts" and products from the refining process where the processing conditions are likely to produce larger aromatic "raft" structures. Utilizing high-resolution mass spectroscopy it is possible to determine the elemental composition of the pyrogram peaks. Utilizing this methodology to generate possible fragments allows us to have more realistic components from which construction of models than from "average structures" which do not demonstrate the structural diversity within the asphaltene. This may be important if only certain structures or certain sizes of structures are responsible for the negative (or positive) aspects of the asphaltene.

Based on the elemental analysis and vapor pressure osmometry the average molecular structure should contain  $C_{77}H_{86}N_1S_{2.6}O_1$  (VPO mw = 1,020 AMU) and  $C_{176}H_{213}N_5S_{6.5}O_{6.5}$  (VPO mw = 2,468 AMU) for Cold Lake and Athabasca  $C_7$ -asphaltenes, respectively. This is comparable with previous work for the Athabasca asphaltene (mw 2,618(2), and 2,750(3)), and for the Cold Lake asphaltene (mw 2,030(3)). However, there is poor agreement between average molecular weights determined by different techniques: laser desorption mass spectroscopy and by VPO(4). The

indication being that either VPO measurements yield molecular weights of strongly bound associations of smaller asphaltene structures or that laser desorption mass spectroscopy fragments larger structures, or does not analyze large structures. The average molecular weights reported here are consistent with the range found by electron impact high-resolution mass spectroscopy of a Mayan (vacuum resid) asphaltene(4). However, the mass spectra technique is known to underestimate the molecular weight, the issue of contention is, by how much? Identification of small multi ring systems is consistent with the general average structural interpretation away from very large aromatic "rafts" structures to smaller sized entities(5). A range of molecular weights and their relative abundance are shown in Table 1. Both asphaltenes are similar in their maximum abundance's in the 300-600 AMU range (74 and 77% or the relative abundance for Cold Lake and Athabasca, respectively). Cold lake has a contribution in the larger mass range (>1,000 AMU) in comparison to the Athabasca asphaltene. The Cold Lake asphaltene has slightly more low-molecular weight material also in comparison to the Athabasca sample.

Previously, identification of electron ionized fragments of an asphaltene was reported to be in good agreement with the traditional elemental analysis, with the aromaticity being slightly underestimated(4) which significantly aids the validity of this type of approach. However, in that study over 90 % of the material was volatilized, while laser desorption in this study volatilized only a small fraction of the asphaltene. Here, only 100 or so of the major peaks have been examined. Furthermore, some calculated elemental assignments were equally valid so there was certain operator bias. The calculated atomic H/C ratios for the Cold Lake sample are shown in Table 1. The weighted atomic H/C ratio of 1.2 is in agreement with the bulk elemental for Cold Lake asphaltene. However, the calculated elemental composition over reports the heteroatom content for sulfur, nitrogen and oxygen (normalized to 100 carbon atoms bulk analysis is  $C_{100}H_{120}N_3S_4O_2$  while the calculated weighted elemental composition is  $C_{100}H_{116}N_3S_5O_3$ ). Additional calibration standards in the laser high-resolution mass spectroscopy might aid in closing this discrepancy.

Size-exclusion chromatography of Athabasca bitumen produced size fractions with essentially the same atomic H/C ratios of 1.4 over a molecular weight range of 900 to 3,000 AMU, (as measured by VPO(6)). A similar trend is seen over the much smaller mass range examined here for the Cold Lake asphaltene. This implies that the higher molecular weight structures are not undergoing circular ring condensation, as it would result in a significant reduction in the H/C ratios. Rather, it seems likely that higher molecular weight structures comprise of lower molecular weight structures linked together via sulfur, oxygen, and aliphatic chains(7) or directly via aryl-aryl bonds. Hence the approach of Murgich et al(8) of stinging small structures together without ring growth to produce an interconnected "island structure" seems reasonable. However, selection of these "binding structures" will have a significant influence on the structural model and their "behavior" and "coke formation" potential. It is the ultimate aim of structural modeling not only to present the structural features that are present in the asphaltene, essential the representation of chemical structure, but also the physical structure and provide a rational explanation of processing behavior occurring during cracking or hydrocracking. For example the Athabasca asphaltene sulfur linkages might be more important "binding structures" than in Cold Lake asphaltene which has a higher coke yield (55.4 in comparison to 47% (daf) for Athabasca). However, many other structural features such as differences in molecular weight distributions or differences in the fine chemical structure are also likely contributors. The current state of knowledge regarding Athabasca structural features is eloquently presented in the literature(7). Aromaticity results have been reported in the literature and are the same for both samples (0.49) for the  $C_7$ -extracted asphaltene(3). The for the same sample the aliphatic hydrogen to carbon ratios were also in close agreement 2.16 and 2.10 for the Athabasca and Cold Lake asphaltenes, respectively(3). Hence, average parameters although useful in comparing materials do not necessarily provide insight into the behavior of the material. Molecular models produced should bare this in mind and should aim to produce chemically, physically accurate models with appropriate "reactivity" to processing.

## CONCLUSIONS

Laser desorption high-resolution mass spectroscopy yielded information regarding the distribution of molecular mass in the range 100 to 1,500 AMU's for Cold Lake and Athabasca asphaltenes. Despite being close in bulk chemical composition (elemental analysis, carbon aromaticity) the asphaltenes differ in coking potential (as determined by thermogravimetric analysis). There are slight differences in the molecular weight distribution between the asphaltene samples. Cold lake has higher molecular weight material in the region of 1,000 to 1,500 amu in comparison to the Athabasca asphaltene, which has no significant contribution for molecular weights greater than 1,000 amu (in the analytical window of this technique). Weighted average molecular weights are 523 and 463 for the Cold Lake and Athabasca asphaltenes, respectively. This shows the opposite trend from vapor pressure osmometry, which yielded average molecular weights of 1,020 and 2,468 for the Cold Lake and Athabasca asphaltenes, respectively. Elemental analysis of carbon and hydrogen for Cold Lake was in reasonable agreement with calculated elemental analysis from high-resolution mass spectroscopy, however, other heteroatoms (S, O and N) were overestimated.

## ACKNOWLEDGEMENTS

Thanks to A. Daniel Jones (Director, Penn State Intercollegiate Center for Mass Spectrometry) for running the laser desorption mass spectroscopy system and assistance in its interpretation.

# REFERENCES

1. ASTM, Designation: D 4530-93, Standard test methods for determination of carbon residue (micro method), in Annual book of ASTM standards, Section 5, Petroleum products, lubricants and fossil fuels, 1998, 919.
2. Kotlyar, L. S., Ripmeester, J. A., Sparks, B. D. and Woods, J., *Fuel*, 1988, **67**, (11), 1529.
3. Suzuki, T., Itoh, M., Takegami, Y. and Watanabe, Y., *Fuel*, 1982, **61**, (5), 402.
4. Hunt, J. E. and Winans, R. E., *Am. Chem. Soc., Div. Fuel Chem. Prepr.*, 1997, **42**, (2), 427.
5. Artok, L., Su, Y., Hirose, Y., Hosokawa, M., Murata, S. and Nomura, M., *Energy & Fuels*, 1999, **13**, (2), 287.
6. Domin, M., Herod, A., Kandiyoti, R., Larsen, J. W., Lazaro, M. -J., Li, S. and Rahimi, P., *Energy & Fuels*, 1999, As soon as publishable web release, ef980065b, [http://pubs.acs.org/subscribe/journals/enfuem/browse\\_asap.html](http://pubs.acs.org/subscribe/journals/enfuem/browse_asap.html).
7. Strausz, O. P., Mojelsky, T. W., Faraji, F., Lown, E. M. and Peng, P., *Energy & Fuels*, 1999, **13**, (2), 207.
8. Murgich, J., Abanero, J. A. and Strausz, O. P., *Energy & Fuels*, 1999, **13**, (2), 278.

Table 1. Molecular Ion Distribution and Average H/C ratio as Determined from High-Resolution Laser Desorption

M/z Range	Cold Lake %	Cold Lake H/C ratio*	Athabasca %
100-199	2		0
200-299	4	0.9	1
300-399	27	1.0	27
400-499	29	1.3	31
500-599	18	1.3	19
600-699	8	1.3	11
700-799	4	1.3	6
800-899	3		3
900-999	2		2
1,000-1,099	1		0
1,100-1,199	1		0
1,200-1,299	1		0
1,300-1,399	1		0
1,400-1,499	1		0
1,500-1,599	0		0
Average mw	523	Weighted H/C= 1.2	463

\*Analysis of at least 10 major fragments in each average H/C calculation

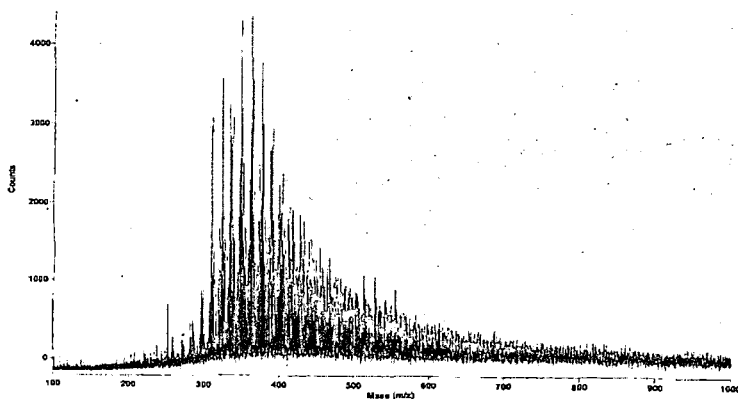


Figure 1. Laser Pyrolysis, High Resolution Mass Spectra Pyrogram of Athabasca Asphaltene